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A

UTILITY PATENT APPLICATION TRANSMITTAL
(Small Entity)

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Docket No.
23267/15D1

Total Pages in this Submission
46

jc571 U.S. PTO 04/22/99

jc618 U.S. PTO 09/296217 04/22/99

TO THE ASSISTANT COMMISSIONER FOR PATENTS
Box Patent Application
Washington, D.C. 20231

Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

Well Lost Circulation Additive, Lost Circulation Treatment Fluid Made Therefrom, Method of Minimizing Lost Circulation In A Subterranean Formation

and invented by:

Boyce D. Burts, Jr.

If a CONTINUATION APPLICATION, *check appropriate box and supply the requisite information:*

☐ **Continuation** ☒ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: **08/962,215**

Which is a:

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: _____

Which is a:

☐ **Continuation** ☐ **Divisional** ☐ **Continuation-in-part (CIP)** of prior application No.: _____

Enclosed are:

Application Elements

1. ☒ Filing fee as calculated and transmitted as described below
2. ☒ Specification having 44 pages and including the following:
   - a. ☒ Descriptive Title of the Invention
   - b. ☒ Cross References to Related Applications *(if applicable)*
   - c. ☐ Statement Regarding Federally-sponsored Research/Development *(if applicable)*
   - d. ☐ Reference to Microfiche Appendix *(if applicable)*
   - e. ☒ Background of the Invention
   - f. ☒ Brief Summary of the Invention
   - g. ☐ Brief Description of the Drawings *(if drawings filed)*
   - h. ☒ Detailed Description
   - i. ☒ Claim(s) as Classified Below
   - j. ☒ Abstract of the Disclosure

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Application Elements (Continued)

3. ☐ Drawing(s) *(when necessary as prescribed by 35 USC 113)*

   a. ☐ Formal b. ☐ Informal Number of Sheets _____

4. ☒ Oath or Declaration

   a. ☐ Newly executed *(original or copy)* ☐ Unexecuted

   b. ☒ Copy from a prior application (37 CFR 1.63(d)) *(for continuation/divisional application only)*

   c. ☒ With Power of Attorney ☐ Without Power of Attorney

   d. ☐ *DELETION OF INVENTOR(S)*
   Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. 1.63(d)(2) and 1.33(b).

5. ☐ Incorporation By Reference *(usable if Box 4b is checked)*
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

6. ☐ Computer Program in Microfiche

7. ☐ Genetic Sequence Submission *(if applicable, all must be included)*

   a. ☐ Paper Copy

   b. ☐ Computer Readable Copy

   c. ☐ Statement Verifying Identical Paper and Computer Readable Copy

Accompanying Application Parts

8. ☐ Assignment Papers *(cover sheet & documents)*

9. ☐ 37 CFR 3.73(b) Statement *(when there is an assignee)*

10. ☐ English Translation Document *(if applicable)*

11. ☐ Information Disclosure Statement/PTO-1449 ☐ Copies of IDS Citations

12. ☒ Preliminary Amendment

13. ☒ Acknowledgment postcard

14. ☒ Certificate of Mailing

    ☐ First Class ☒ Express Mail *(Specify Label No.):* **EL 167 748 141 US**

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Accompanying Application Parts (Continued)

15. ☐ Certified Copy of Priority Document(s) *(if foreign priority is claimed)*

16. ☒ Small Entity Statement(s) - Specify Number of Statements Submitted: 1

17. ☐ Additional Enclosures *(please identify below):*

Fee Calculation and Transmittal

CLAIMS AS FILED

For	#Filed	#Allowed	#Extra		Rate	Fee
Total Claims		- 20 =	0	x	$11.00	$0.00
Indep. Claims		- 3 =	0	x	$41.00	$0.00
Multiple Dependent Claims (check if applicable) ☐						$0.00
					BASIC FEE	$380.00
OTHER FEE *(specify purpose)*						$380.00
					TOTAL FILING FEE	$380.00

☒ A check in the amount of **$380.00** to cover the filing fee is enclosed.

☒ The Commissioner is hereby authorized to charge and credit Deposit Account No. **07-1245** as described below. A duplicate copy of this sheet is enclosed.

- ☐ Charge the amount of as filing fee.
- ☒ Credit any overpayment.
- ☒ Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.
- ☐ Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).

Dated: **April 22, 1999**

Signature

J. M. (Mark) Gilbreth, Reg. No. 33,388
Attorney for Applicant

cc:

P01USML/REV03

Applicant or Patentee: Boyce D. Burts, Jr. Attorney's Docket No.: 23267/15
Serial or Patent No.: 08/962,215
Filed or Issued: October 31, 1997
For: *Lost Circulation Additive, Lost Circulation Treatment Fluid Made Therefrom, And Method of Minimizing Lost Circulation in a Subterranean Formation*

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) and 1.27(c)) - SMALL BUSINESS CONCERN

I hereby declare that I am

[ ] the owner of the small business concern identified below:
[X] an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN **Bottom Line Industries, Inc.**
ADDRESS OF CONCERN **P. O. Box 82007**
Lafayette, Louisiana 70598-2007

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled as named above and by inventor as named above described in

[ ] the specification filed herewith
[X] Application Serial No. 08/962,215 filed October 31, 1997.
[ ] patent no. _____, issued _____

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(d) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING **Boyce D. Burts, Jr.**
TITLE OF PERSON OTHER THAN OWNER President
ADDRESS OF PERSON SIGNING 300 Running Deer Drive, Maurice, LA 70555
SIGNATURE Boyce D. Burts DATE 4/1/98

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: Boyce D. Burts, Jr.	§	**ART UNIT NO.: 3672**
	§	
FILED:	§	
	§	
SERIAL NO.:	§	**EXAMINER: Suchfield, George**
	§	
TITLE: ***Lost Circulation Additive, Lost Circulation Treatment Fluid Made Therefrom, And Method of Minimizing Lost Circulation in a Subterranean Formation***	§	**ATTORNEY DOCKET NO.: 23267/15D1**

The Assistant Commissioner of Patents
Washington, DC 20231

PRELIMINARY AMENDMENT

Dear Sir:

Please enter the Preliminary Amendment prior to calculation of the filing fee. The following amendments and remarks are respectfully submitted:

AMENDMENTS

Please cancel claims 14-33.

REMARKS

Applicant hereby requests prosecution of claims 1-13 (non-elected in the parent application), drawn to a composition and method for preparing, classified in class 507, subclass 104.

Respectfully submitted,

Date: **April 22, 1999**

J. M. (Mark) Gilbreth, Reg. No. 33,388
Attorney for Applicant

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713/227-1200

Express Mail Label No.: EL 167 748 141 US

PATENT SPECIFICATION

TITLE: LOST CIRCULATION ADDITIVE, LOST CIRCULATION TREATMENT FLUID MADE THEREFROM, AND METHOD OF MINIMIZING LOST CIRCULATION IN A SUBTERRANEAN FORMATION

INVENTOR: BOYCE D. BURTS, JR.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to lost circulation additives, to lost circulation treatment fluids made therefrom, to methods of minimizing lost circulation in a well. In another aspect, the present invention relates to lost circulation additives comprising polymer and fibers or comminuted plant materials, to lost circulation treatment fluids made therefrom, to methods of minimizing lost circulation in a well using such fluids.

2. Description of the Related Art

Subterranean wells are utilized to reach desirable oil and/or gas bearing formations, and are generally drilled utilizing rotary drilling techniques. In such rotary drilling of wells for oil and gas, drilling fluids ("muds") are circulated into the well through hollow tubular drill pipe, past the teeth of the cutter head to sweep away the cuttings from the cutter head, and returned to the surface along with the cuttings through the annulus surrounding the drill pipe. The drilling fluid is generally circulated in such a manner as to remove drill cuttings to prevent clogging of the cutter and to support the walls of the well hole. Such drill cuttings are entrained in the drilling fluid and brought to the surface with the fluid and then screened out and discarded. In addition to removing drill cuttings and supporting the walls of the well hole, the drilling fluid also serves to cool and lubricate the drill bit and, in the case of systems employing downhole drill motors, it functions as a power fluid for the drill motor.

Typically, drilling fluids may be water-base,

employing a base of fresh water, salt water, or an oil-in-water emulsion in which water forms the continuous phase, or oil-base, employing a relatively pure oil such as crude petroleum oil or diesel oil, or in may be an "invert" emulsion, a water-in-oil emulsion in which oil forms the continuous phase or a synthetic base employing a polymer.

Drilling fluids normally contain clays and/or other dispersed solids which are employed to impart desired rheological properties to the drilling fluid. Not only do these clays and/or other suspended solids impart desirable thixotropic properties to the drilling fluid, they also serve to coat the walls of the well with a relatively impermeable sheath, commonly termed a filter cake, which retards the flow of fluid from the well into the surrounding subterranean formations.

In addition to clays and/or other suspended particles, a drilling fluid may also contain one or more weighting agents which function to increase the density of the fluid to a level which will offset high pressures encountered during the drilling operation. Non-limiting

examples of suitable weighting agents which may be used in either water base or oil base drilling fluids include heavy minerals such as barite and gelena.

One problem very commonly encountered during rotary drilling operations is the problem of lost circulation in which part or all of the drilling fluid is not returned to the surface. This problem may manifest itself anywhere from moderate losses of the drilling fluid, to substantial or even total losses of the drilling fluid such that little or none of it is returned to the surface. Where a formation zone is identified in which unacceptably large amounts of drilling fluid is lost, such formation zone is commonly termed a "loss zone" or a loss circulation zone." While there are many causes for loss circulation, non-limiting examples include those situations when the well encounters a formation of unusually high permeability or one which has naturally occurring horizontal or vertical fractures or fissures. Also, the formation may be fractured accidentally by the hydrostatic pressure exerted by the drilling mud,

particularly when a change over to a relatively heavy mud is made in order to control high formation pressures.

As can be expected, over the years numerous techniques have been developed to prevent or reduce loss circulation. One common technique where the loss circulation is not so severe is to add various fluid loss agents which function to change the rheological properties of the drilling mud in order to increase its resistence to flow from the well bore into the formation. Such fluid loss agents include synthetic polymeric thickening agents such as partially hydrolyzed polyacrylamide, polyelectrolite such as an ionic polysaccharide, various gums such as locust bean gum and guar gum, various starches, and carboxymethylcellulose (CMC) or carboxyethylcellulose (CEC).

Where the loss circulation is more severe, it is a normal practice to incorporate into the drilling mud various bulk materials which function to combat or prevent loss circulation. It has been common in the past to add any number of materials to the drilling fluid which act to reduce or prevent flow of the drilling fluid

from the well hole to the formation. These materials are commonly referred to as "loss (or lost) circulation additives". Such prior art loss circulation materials include fibrous, flake (or laminated), and granular materials. A nonexhaustive list of such loss circulation includes nut and seed shells or hulls (peanut almond, walnut, peach, brazil, coconut, peanut, sunflower, flax, cocoa bean, cottonseed, rice, linseed); crude pectate pulp; feathers; citrus pulp; beet pulp; peat moss fibers; jute; flax; mohair; lechuguilla fibers; cotton; cotton linters; wool; paper; wet-strength paper; sugar cane; bagasse; bamboo; corn stalks; sawdust; straw; wood fiber; cedar fiber; bark chips; cork; popped popcorn; dehydrated vegetable matter (suitably dehydrated carbohydrates such as citrus pulp, oatmeal, tapioca, rice grains, potatoes, carrots, beets, and various grain sorghams); the ground woody ring portion of corn cobs; whole ground corn cobs; hydrophobic, organophilic, water-wettable fibrous materials such as treated cotton, dried bagasse, and dried peat fibers; and specific mixtures of these

materials. Many assorted inorganic materials have also been utilized as loss circulation materials.

Seepage losses can occur to any type of loss zone and in any type of formation when the particles in the drilling fluid are not fine enough to complete the seal. It has been established that the maximum allowable drilling fluid loss is on the order of 1 bbl/hr ($0.16m^3/h$), as measured in the mud pit at the surface.

There are numerous examples of patents teaching the use of various types of materials for use as lost circulation additives in drill fluids. The following are not an exhaustive sampling.

U.S. Patent No. 2,610,149, issued September 9, 1952, to Van Dyke, discloses the use of corn stalks, wood shavings, flake cellophane and chopped up paper in drilling fluids.

U.S. Patent No. 2,779,417, issued January 29, 1957, to Clark et al., discloses the use of cellophane, rice hulls and shredded paper as bridging agents in a well fluid.

U.S. Patent No. 4,247,403, issued January 27, 1981, to Foley et al., discloses the use of whole corncobs or the woody ring portion of corncobs as loss circulation additives for drilling fluids.

U.S. Patent No. 4,474,665, issued October 2, 1984 to Green, discloses a lost circulation material useful in drilling fluids formed from cocoa bean shell material having a particle size distribution from 2 to 100 mesh.

U.S. Patent No. 4,579,668, issued April 1, 1986 to Messenger, discloses for use as drilling fluid bridging agents, ground walnut shells, cellophane and shredded wood.

U.S. Patent No. 5,004,553, issued April 2, 1991, and U.S. Patent No. 5,071,575, issued December 10, 1991, both to House et al., disclose a well working composition containing oat hulls and optionally including one or more of ground corn cobs, cotton, citrus pulp, and ground cotton burrs.

U.S. Patent No. 5,076,944, issued December 31, 1991 to Cowan et al., discloses a seepage loss additive comprising ground cotton burrs in combination with one or

more of ground oat hulls, ground corn cobs, cotton, ground citrus pulp, ground peanut shells, ground rice hulls, and ground nut shells.

U.S. Patent No. 5,118,664, issued June 2, 1992, and U.S. Patent No. 5,599,776, issued February 4, 1997, both to Burts, Jr., disclose the use of various comminuted plant materials as lost circulation materials.

U.S. Patent No. 4,957,166, issued September 18, 1990 to Sydansk, discloses the use of a water soluble carboxylate crosslinking polymer along with a chromic carboxylate complex crosslinking agent as a lost circulation material. Sydansk further teaches that the performance requirements of conformance improvement treatment polymers are different from those of lost circulation polymers. Thus, while U.S. Patent No. 5,377,760, issued January 3, 1995 to Merrill discloses addition of fibers to an aqueous solution of partially hydrolyzed polyacrylamide polymer, with subsequent injection into the subterranean to improve conformance, Sydansk teaches that such would not necessarily work for lost circulation treatment.

Additionally, Merrill's conformance treatment method of mixing the fibers with the polymer solution followed by injection, requires a multiplicity of storage and mixing tanks, and a metering system which must be operated during the operation of the well. Specifically, a first tank will store a water and polymer solution, a second tank will store a water and cross-linking solution, and a third tank will be used to mix fibers with polymer solution from the first tank to create a polymer/fiber slurry. This polymer/fiber slurry is then metered from the third tank and combined with cross-linking solution metered from the second tank to the well bore.

Thus, in spite of the advancements in the prior art, there still need for further innovation in the lost circulation additives.

There is need for further innovation for lost circulation additives utilizing a water soluble polymer.

There is another need for a lost circulation additive which would allow for simplification of the mixing equipment.

These and other needs in the art will become apparent to those of skill in the art upon review of this specification, including its drawings and claims.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide for further innovation in lost circulation additives.

It is an another object of the present invention to provide for further innovation for lost circulation additives utilizing a water soluble polymer.

It is even another object of the present invention to provide for a lost circulation additive which would allow for simplification of the mixing equipment.

These and other objects of the present invention will become apparent to those of skill in the art upon review of this specification, including its drawings and claims.

According to one embodiment of the present invention there is provided a lost circulation additive comprising a dry mixture of water soluble crosslinkable polymer, a crosslinking agent, and a reinforcing material selected from among fibers and comminuted plant materials. In preferred embodiments, the polymer is an a carboxylate-containing polymer and the crosslinking agent is a

chromic carboxylate complex. In other preferred embodiments, the reinforcing material may comprise hydrophobic fibers selected from among nylon, rayon, and hydrocarbon fibers, and/or hydrophilic fibers selected from among glass, cellulose, carbon, silicon, graphite, calcined petroleum coke, and cotton fibers. The comminuted plant material is selected from the group of comminuted plant materials of nut and seed shells or hulls of almond, brazil, cocoa bean, coconut, cotton, flax, grass, linseed, maize, millet, oat, peach, peanut, rice, rye, soybean, sunflower, walnut, and wheat; rice tips; rice straw; rice bran; crude pectate pulp; peat moss fibers; flax; cotton; cotton linters; wool; sugar cane; paper; bagasse; bamboo; corn stalks; sawdust; wood; bark; straw; cork; dehydrated vegetable matter; whole ground corn cobs; corn cob light density pith core; corn cob ground woody ring portion; corn cob chaff portion; cotton seed stems; flax stems; wheat stems; sunflower seed stems; soybean stems; maize stems; rye grass stems; millet stems; and mixtures thereof.

According to another embodiment of the present invention, there is provided a method of forming a lost circulation fluid. The method generally includes taking the above lost circulation additive and contacting it with water or other aqueous solution.

According to even another embodiment of the present invention, there is provided a method of preventing lost circulation. The method generally includes contacting the above described lost circulation additive with water or an aqueous solution to form a lost circulation fluid. The method then includes injecting the lost circulation fluid into the formation.

These and other embodiments of the present invention will become apparent to those of skill in the art upon review of this specification and claims.

DETAILED DESCRIPTION OF THE INVENTION

The lost circulation additive of the present invention includes polymer, cross-linking agent and either fibers or comminuted particles of plant materials. In a preferred embodiment of the present invention, the lost circulation additive is a dry mixture of polymer, cross-linking agent and either fibers or comminuted particles of plant materials.

Any suitable relative amounts of the polymer, cross-linking agent and either fibers or comminuted particles of plant materials may be utilized in the present invention provided that the desired lost circulation results are achieved. Generally, the fibers or comminuted particles will comprise in the range of about 1 to about 99 weight percent, preferably in the range of about 25 to about 90 weight percent, more preferably in the range of about 50 to about 80 weight percent, and even more preferably in the range of about 70 to about 75 weight percent, all based on the total with of the polymer, fibers and particles. A suitable amount of crosslinking agent is provided to reach the desired

amount of crosslinking. Suitable amounts of dispersants, retarders, accelerents, and other additives may be provided as necessary or desired.

The polymer utilized in the practice of the present invention is preferably water soluble and must be capable of being pumped as a liquid and subsequently crosslinked in place to form a substantially non-flowing crosslinked polymer which has sufficient strength to withstand the pressures exerted on it. Moreover, it must have a network structure capable of incorporating reinforcing fibers.

While any suitable water soluble polymer may be utilized, the preferred polymer utilized in the practice of the present invention is a carboxylate-containing polymer. This preferred carboxylate-containing polymer may be any crosslinkable, high molecular weight, water-soluble, synthetic polymer or biopolymer containing one or more carboxylate species.

The average molecular weight of the carboxylate-containing polymer utilized in the practice of the present invention is in the range of about 10,000

to about 50,000,000, preferably in the range of about 100,000 to about 20,000,000, and most preferably in the range of about 200,000 to about 15,000,000.

Biopolymers useful in the present invention include polysaccharides and modified polysaccharides. Non-limiting examples of biopolymers are xanthan gum, guar gum, carboxymethylcellulose, o-carboxychitosans, hydroxyethylcellulose, hydroxypropylcellulose, and modified starches. Non-limiting examples of useful synthetic polymers include acrylamide polymers, such as polyacrylamide, partially hydrolyzed polyacrylamide and terpolymers containing acrylamide, acrylate, and a third species. As defined herein, polyacrylamide (PA) is an acrylamide polymer having substantially less than 1% of the acrylamide groups in the form of carboxylate groups. Partially hydrolyzed polyacrylamide (PHPA) is an acrylamide polymer having at least 1%, but not 100%, of the acrylamide groups in the form of carboxylate groups. The acrylamide polymer may be prepared according to any conventional method known in the art, but preferably has the specific properties of acrylamide polymer prepared

according to the method disclosed by U.S. Pat. No. Re. 32,114 to Argabright et al incorporated herein by reference.

Any crosslinking agent suitable for use with the selected polymer may be utilized in the practice of the present invention. Preferably, the crosslinking agent utilized in the present invention is a chromic carboxylate complex.

The term "complex" is defined herein as an ion or molecule containing two or more interassociated ionic, radical or molecular species. A complex ion as a whole has a distinct electrical charge while a complex molecule is electrically neutral. The term "chromic carboxylate complex" encompasses a single complex, mixtures of complexes containing the same carboxylate species, and mixtures of complexes containing differing carboxylate species.

The chromic carboxylate complex useful in the practice of the present invention includes at least one or more electropositive chromium III species and one or more electronegative carboxylate species. The complex

may advantageously also contain one or more electronegative hydroxide and/or oxygen species. It is believed that, when two or more chromium III species are present in the complex, the oxygen or hydroxide species may help to bridge the chromium III species. Each complex optionally contains additional species which are not essential to the polymer crosslinking function of the complex. For example, inorganic mono- and/or divalent ions, which function merely to balance the electrical charge of the complex, or one or more water molecules may be associated with each complex. Non-limiting representative formulae of such complexes include:

$[Cr_3(CH_3CO_2)_6(OH)_2]^{1+}$;

$[Cr_3(CH_3CO_2)_6(OH)_2]NO_3 \bullet 6H_2O$;

$[Cr_3(CH_3CO_2)_6(OH)_2]^{3+}$; and

$[Cr_3(CH_3CO_2)_6(OH)_2](CH_3CO_2)_3 \bullet H_2O$.

"Trivalent chromium" and "chromic ion" are equivalent terms encompassed by the term "chromium III" species as used herein.

The carboxylate species are advantageously derived from water-soluble salts of carboxylic acids, especially low molecular weight mono-basic acids. Carboxylate species derived from salts of formic, acetic, propionic, and lactic acid, substituted derivatives thereof and mixtures thereof are preferred. The preferred carboxylate species include the following water-soluble species: formate, acetate, propionate, lactate, substituted derivatives thereof, and mixtures thereof. Acetate is the most preferred carboxylate species. Examples of optional inorganic ions include sodium, sulfate, nitrate and chloride ions.

A host of complexes of the type described above and their method of preparation are well known in the leather tanning art. These complexes are described in Shuttleworth and Russel, Journal of the Society of Leather Trades' Chemists, "The Kinetics of Chrome Tannage Part I.," United Kingdom, 1965, v. 49, p. 133-154; "Part III.," United Kingdom, 1965, v. 49, p. 251-260; "Part IV.," United Kingdom, 1965, v. 49, p. 261-268; and Von Erdman, Das Leder, "Condensation of Mononuclear Chromium

(III) Salts to Polynuclear Compounds," Eduard Roether Verlag, Darmstadt Germany, 1963, v. 14, p. 249; and incorporated herein by reference. Udy, Marvin J., Chromium. Volume 1: Chemistry of Chromium and its Compounds. Reinhold Publishing Corp., N.Y., 1956, pp. 229-233; and Cotton and Wilkinson, Advanced Inorganic Chemistry 3rd Ed., John Wiley and Sons, Inc., N.Y., 1972, pp. 836-839, further describe typical complexes which may be within the scope of the present invention and are incorporated herein by reference. The present invention is not limited to the specific complexes and mixtures thereof described in the references, but may include others satisfying the above-stated definition.

Salts of chromium and an inorganic monovalent anion, e.g., CrCl3, may also be combined with the crosslinking agent complex to accelerate gelation of the polymer solution, as described in U.S. Pat. No. 4,723,605 to Sydansk, which is incorporated herein by reference.

The molar ratio of carboxylate species to chromium III in the chromic carboxylate complexes used in the process of the present invention is typically in the

range of 1:1 to 3.9:1. The preferred ratio is range of 2:1 to 3.9:1 and the most preferred ratio is 2.5:1 to 3.5:1.

The additive of the present invention may comprise fibers or comminuted particles of plant materials, and preferably comprises comminuted particles of one or more plant materials.

Fibers suitable for use in the present invention are selected from among hydrophilic and hydrophobic fibers. Incorporation of hydrophobic fibers will require use of a suitable wetting agent. Preferably, the fibers utilized in the present invention comprise hydrophilic fibers, most preferably both hydrophilic and hydrophobic fibers.

With respect to any particular fiber employed in the practice of the present invention, it is believed that the longer the fiber, the more difficult it is to be mixed uniformly in solution. It is believed that fibers as long as 12,500 microns may tend to aggregate and form clumps. The shorter the fiber, it is believed the easier it is to mix in solution. On the other hand, the shorter

the fiber, the greater the quantity necessary to provide the desired level of strength in a reinforced mature gel. In general, the fibers utilized in the present invention will have a length in the range of 100 microns to 3200 microns, preferable 100 microns to 1000 microns.

Non-limiting examples of suitable hydrophobic fibers include nylon, rayon, hydrocarbon fibers and mixtures thereof.

Non-limiting examples of suitable hydrophilic fibers include glass, cellulose, carbon, silicon, graphite, calcined petroleum coke, cotton fibers, and mixtures thereof.

Non-limiting examples of comminuted particles of plant materials suitable for use in the present invention include any derived from: nut and seed shells or hulls such as those of peanut, almond, brazil, cocoa bean, coconut, cotton, flax, grass, linseed, maize, millet, oat, peach, peanut, rice, rye, soybean, sunflower, walnut, wheat; various portions of rice including the rice tips, rice straw and rice bran; crude pectate pulp; peat moss fibers; flax; cotton; cotton linters; wool;

sugar cane; paper; bagasse; bamboo; corn stalks; various tree portions including sawdust, wood or bark; straw; cork; dehydrated vegetable matter (suitably dehydrated carbonhydrates such as citrus pulp, oatmeal, tapioca, rice grains, potatoes, carrots, beets, and various grain sorghams); whole ground corn cobs; or various plant portions the corn cob light density pith core, the corn cob ground woody ring portion, the corn cob coarse or fine chaff portion, cotton seed stems, flax stems, wheat stems, sunflower seed stems, soybean stems, maize stems, rye grass stems, millet stems, and various mixtures of these materials.

Optionally, dispersant for comminuted plant material will be utilized the in the range of about 1 to about 20 pounds, preferably in the range of about 5 to about 10 pounds, and more preferably in the range of about 7 to about 8 pounds of dispersant may be utilized per pound of comminuted plant material. A non-limiting example of a suitable dispersant is NaCl.

Preferred comminuted materials useful in the practice of the present invention include those derived

from peanuts, wood, paper any portion of rice seed or plant, and any portion of corn cobs.

These various materials can be comminuted to very fine particle sizes by drying the products and using hammer mills, cutter heads, air control mills or other comminution methods as is well known to those of skill in the comminution art. Air classification equipment or other means can be used for separation of desired ranges of particle sizes using techniques well-known in the comminution art.

Any suitable size of comminuted material may be utilized in the present invention, along as such size produces results which are desired. In most instances, the size range of the comminuted materials utilized herein will range from below about 8 mesh ("mesh" as used herein refers to standard U.S. mesh), preferably from about -65 mesh to about -100 mesh, and more preferably from about -65 mesh to about -85 mesh. Specifically preferred particle sizes for some materials are provided below.

Preferred mixtures of comminuted materials useful in the practice of the present invention include a rice fraction and peanut hulls; a rice fraction and wood fiber and/or almond hulls; a rice fraction and a corn cob fraction, preferably a chaff portion; and a corn cob fraction, preferably a pith or chaff portion, a rice fraction, and at least one of wood fiber, nut shells, paper and shredded cellophane.

Rice is commercially available in the form of rice hulls, rice tips, rice straw and rice bran, as these various parts of the rice plant are separated commercially and are widely available from rice mills. Preferably, the size range of the rice fraction utilized herein will range from below about 8 mesh ("mesh" as used herein refers to standard U.S. mesh), preferably from about -65 mesh to about -100 mesh, and more preferably from about -65 mesh to about -85 mesh.

After the corn kernels are removed, corn cobs consist of four principle parts that are arranged concentrically. The central portion is a very light density pith core, that is surrounded by a woody ring,

that in turn is surrounded by a coarse chaff portion, that in turn is covered by a fine chaff portion. The coarse and fine chaff portions form the sockets for anchoring the corn kernels to the corncob. The normal methods of grinding corncobs produce a mixture of all four parts enumerated above. It is possible, however, to separate the woody ring material from the remainder of the cob. The chaff portion of the corncob remaining after removal of the woody ring material is known as "bees wings". In the present invention, any of the pith or chaff portions("BPC") are the preferred portions of the corn cob, with the chaff portions being more preferred. A range of particle sizes of pith and chaff can be obtained from comminution, but the size range smaller than about 8 mesh is suitable for this invention. Preferably, a particle size distribution ranging from smaller than 8 mesh to smaller than 100 mesh is utilized.

Preferred woods for use as comminuted materials in the present invention include any type of hard wood fiber, including cedar fiber, oak fiber, pecan fiber and

elm fiber. Preferably the wood fiber comprises cedar fibers.

Preferred nut shells for use in the present invention include pecan, walnut, and almond. Preferably, the nut shells comprise at least one of pecan or walnut shells.

Preferred particle sizes for the wood fibers, nut shells, paper and cellophane will generally range from about +10 mesh to -100 mesh. An illustration of a non-limiting particle size distribution for these materials would include particles of +10 mesh, +20 mesh, +30 mesh, +50 mesh, +60 mesh, +100 mesh, and -100 mesh.

For one of the preferred comminuted plant mixtures comprising a corn cob fraction, a rice fraction, and at least one of wood fiber, nut shells, paper and shredded cellophane, the mixture will generally comprise in the range of about 5 to about 95 weight percent rice, in the range of about 5 to about 95 weight percent corncob pith or chaff, with the total of ground wood fiber, ground nut shells, ground paper and shredded cellophane comprising in the range of about 5 to about 95 weight percent

(weight percent based on the total weight of plant material in the mixture. Preferred ranges are about 20 to about 75 weight percent rice, about 5 to about 35 weight percent corncob pith or chaff, with the total of ground wood fiber, ground nut shells, ground paper and shredded cellophane comprising in the range of about 20 to about 75 weight percent. More preferred ranges are about 30 to about 50 weight percent rice, about 10 to about 30 weight percent corncob pith and chaff, with the total of ground wood fiber, ground nut shells, ground paper and shredded cellophane comprising in the range of about 25 to about 50 weight percent.

As these comminuted materials are to be added to a water base lost circulation fluid, a small amount of oil may optionally added to the mixture. This optional oil is preferably added while the plant materials are being mixed together. This mixing may take place in a ribbon blender, where the oil in the required amount is applied by a spray bar. The oil wets the particles and adds to their lubricity while at the same time helping to control dust produced by the mixing operation. A variety of oils

may be utilized in the practice of the present invention in concentrations generally ranging from about 1 percent to about 5 percent by weight based on the total weight of the mixture of comminuted materials, more preferably ranging from about 1 percent to about 2 percent. A non-limiting example of a commercially available oil suitable for use in the present invention includes ISOPAR V, available from Exxon Corporation.

The various components of the present invention may be mixed in any suitable order utilizing mixing techniques as known to those in the art, including dry mixing of the various components prior to addition to water, or alternatively, either or both of the polymer and cross-linking agent may be utilized as a solution. Most preferably, the various components are mixed in dry form, and then contacted with water or aqueous solution to form a lost circulation fluid. This lost circulation fluid is then injected into the well as is known in the art.

For an example of polymers and crosslinking agents suitable for use herein and details regarding their making and use, please see U.S. Patent Nos. 4,957,166 and 4,989,673, both incorporated herein by reference.

While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which this invention pertains.

I CLAIM:

1. A lost circulation additive comprising a dry mixture of a water soluble crosslinkable polymer, a crosslinking agent, and a reinforcing material selected from among fibers and comminuted plant materials.

2. The additive of claim 1 wherein the polymer is an a carboxylate-containing polymer and the crosslinking agent is a chromic carboxylate complex.

3. The additive of claim 2 wherein the reinforcing material comprises hydrophilic and hydrophobic fibers.

4. The additive of claim 3 wherein the hydrophobic fibers comprise at least one selected from the group of hydrophobic fibers consisting essentially of nylon, rayon, and hydrocarbon fibers, and wherein the hydrophilic fibers comprise at least one selected from the group of hydrophilic fibers consisting essentially of

glass, cellulose, carbon, silicon, graphite, calcined petroleum coke, and cotton fibers.

5. The additive of claim 2 wherein the reinforcing material comprises comminuted plant material.

6. The additive of claim 5 wherein the reinforcing material comprises at least one comminuted material selected from the group of comminuted plant materials consisting essentially of nut and seed shells or hulls of almond, brazil, cocoa bean, coconut, cotton, flax, grass, linseed, maize, millet, oat, peach, peanut, rice, rye, soybean, sunflower, walnut, and wheat; rice tips; rice straw; rice bran; crude pectate pulp; peat moss fibers; flax; cotton; cotton linters; wool; sugar cane; paper; bagasse; bamboo; corn stalks; sawdust; wood; bark; straw; cork; dehydrated vegetable matter; whole ground corn cobs; corn cob light density pith core; corn cob ground woody ring portion; corn cob chaff portion; cotton seed stems; flax stems; wheat stems; sunflower seed stems;

soybean stems; maize stems; rye grass stems; millet stems; and mixtures thereof.

7. The additive of claim 2 wherein the polymer is a partially hydrolyzed polyacrylamide.

8. The additive of claim 7 wherein the reinforcing material is a comminuted material selected from among comminuted materials derived from peanuts, wood, paper any portion of rice seed or plant, any portion of corn cobs, and mixtures thereof.

9. The additive of claim 8 wherein the additive further includes cellophane, and wherein the reinforcing material is a comminuted material selected from among mixtures of comminuted rice fraction and peanut hulls; mixtures of comminuted rice fraction, and wood fiber or almond hulls; mixtures of comminuted rice fraction and corn cob fraction; and mixtures of comminuted rice fraction and corn cob fraction and at least one of wood fiber, nut shells, and paper.

10. The additive of claim 9 wherein the reinforcing material comprises comminuted mixture of rice fraction, corn cob pith and chaff, cedar fiber, nut shells, and paper.

11. A method of forming a lost circulation fluid comprising:

(a) providing a lost circulation additive comprising a dry mixture of water soluble crosslinkable polymer, a crosslinking agent, and a reinforcing material selected from among fibers and comminuted plant materials; and

(b) contacting the lost circulation additive with water or an aqueous solution to form the lost circulation fluid.

12. The method of claim 11 wherein the polymer is a partially hydrolyzed polyacrylamide, the crosslinking agent is a chromic carboxylate complex, wherein the additive further includes cellophane, and wherein the

reinforcing material is a comminuted material selected from among mixtures of comminuted rice fraction and peanut hulls; mixtures of comminuted rice fraction, and wood fiber or almond hulls; mixtures of comminuted rice fraction and corn cob fraction; and mixtures of comminuted rice fraction and corn cob fraction and at least one of wood fiber, nut shells, and paper.

13. The additive of claim 12 wherein the reinforcing material comprises comminuted mixture of rice fraction, corn cob pith and chaff, cedar fiber, nut shells, and paper.

14. A method for preventing lost circulation from a borehole into a subterranean formation comprising:

(a) providing a lost circulation additive comprising a dry mixture of water soluble crosslinkable polymer, a crosslinking agent, and a reinforcing material selected from among fibers and comminuted plant materials;

(b) contacting the lost circulation additive with water or an aqueous solution to for a lost circulation fluid; and

(c) injecting the lost circulation fluid into the borehole.

15. The method of claim 14 wherein the polymer is an a carboxylate-containing polymer and the crosslinking agent is a chromic carboxylate complex.

16. The method of claim 15 wherein the reinforcing material comprises hydrophilic and hydrophobic fibers.

17. The method of claim 16 wherein the hydrophobic fibers comprise at least one selected from the group of hydrophobic fibers consisting essentially of nylon, rayon, and hydrocarbon fibers, and wherein the hydrophilic fibers comprise at least one selected from the group of hydrophilic fibers consisting essentially of glass, cellulose, carbon, silicon, graphite, calcined petroleum coke, and cotton fibers.

18. The method of claim 15 wherein the reinforcing material comprises comminuted plant material.

19. The method of claim 18 wherein the reinforcing material comprises at least one comminuted material selected from the group of comminuted plant materials consisting essentially of nut and seed shells or hulls of almond, brazil, cocoa bean, coconut, cotton, flax, grass, linseed, maize, millet, oat, peach, peanut, rice, rye, soybean, sunflower, walnut, and wheat; rice tips; rice straw; rice bran; crude pectate pulp; peat moss fibers; flax; cotton; cotton linters; wool; sugar cane; paper; bagasse; bamboo; corn stalks; sawdust; wood; bark; straw; cork; dehydrated vegetable matter; whole ground corn cobs; corn cob light density pith core; corn cob ground woody ring portion; corn cob chaff portion; cotton seed stems; flax stems; wheat stems; sunflower seed stems; soybean stems; maize stems; rye grass stems; millet stems; and mixtures thereof.

20. The method of claim 15 wherein the polymer is a partially hydrolyzed polyacrylamide.

21. The method of claim 20 wherein the reinforcing material is a comminuted material selected from among comminuted materials derived from peanuts, wood, paper any portion of rice seed or plant, any portion of corn cobs, and mixtures thereof.

22. The method of claim 21 wherein the additive further includes cellophane, and wherein the reinforcing material is a comminuted material selected from among mixtures of comminuted rice fraction and peanut hulls; mixtures of comminuted rice fraction, and wood fiber or almond hulls; mixtures of comminuted rice fraction and corn cob fraction; and mixtures of comminuted rice fraction and corn cob fraction and at least one of wood fiber, nut shells, and paper.

23. The method of claim 22 wherein the reinforcing material comprises comminuted mixture of rice fraction,

corn cob pith and chaff, cedar fiber, nut shells, and paper.

24. A method for decreasing fluid loss from a borehole into a subterranean formation comprising:

(a) providing a lost circulation additive comprising an aqueous solution of water soluble crosslinkable polymer, a crosslinking agent, and a reinforcing material selected from among fibers and comminuted plant materials; and

(b) injecting the lost circulation fluid into the borehole.

25. The method of claim 24 wherein the polymer is an a carboxylate-containing polymer and the crosslinking agent is a chromic carboxylate complex.

26. The method of claim 25 wherein the reinforcing material comprises hydrophilic and hydrophobic fibers.

27. The method of claim 26 wherein the hydrophobic fibers comprise at least one selected from the group of hydrophobic fibers consisting essentially of nylon, rayon, and hydrocarbon fibers, and wherein the hydrophilic fibers comprise at least one selected from the group of hydrophilic fibers consisting essentially of glass, cellulose, carbon, silicon, graphite, calcined petroleum coke, and cotton fibers.

28. The method of claim 25 wherein the reinforcing material comprises comminuted plant material.

29. The method of claim 28 wherein the reinforcing material comprises at least one comminuted material selected from the group of comminuted plant materials consisting essentially of nut and seed shells or hulls of almond, brazil, cocoa bean, coconut, cotton, flax, grass, linseed, maize, millet, oat, peach, peanut, rice, rye, soybean, sunflower, walnut, and wheat; rice tips; rice straw; rice bran; crude pectate pulp; peat moss fibers; flax; cotton; cotton linters; wool; sugar cane; paper;

bagasse; bamboo; corn stalks; sawdust; wood; bark; straw; cork; dehydrated vegetable matter; whole ground corn cobs; corn cob light density pith core; corn cob ground woody ring portion; corn cob chaff portion; cotton seed stems; flax stems; wheat stems; sunflower seed stems; soybean stems; maize stems; rye grass stems; millet stems; and mixtures thereof.

30. The method of claim 25 wherein the polymer is a partially hydrolyzed polyacrylamide.

31. The method of claim 30 wherein the reinforcing material is a comminuted material selected from among comminuted materials derived from peanuts, wood, paper any portion of rice seed or plant, any portion of corn cobs, and mixtures thereof.

32. The method of claim 31 wherein the additive further includes cellophane, and wherein the reinforcing material is a comminuted material selected from among mixtures of comminuted rice fraction and peanut hulls; mixtures of

comminuted rice fraction, and wood fiber or almond hulls; mixtures of comminuted rice fraction and corn cob fraction; and mixtures of comminuted rice fraction and corn cob fraction and at least one of wood fiber, nut shells, and paper.

33. The method of claim 32 wherein the reinforcing material comprises comminuted mixture of rice fraction, corn cob pith and chaff, cedar fiber, nut shells, and paper.

ABSTRACT

For lost circulation treatment, a lost circulation additive including a dry mixture of water soluble crosslinkable polymer, a crosslinking agent, and a reinforcing material of fibers and/or comminuted plant materials. The method of forming a lost circulation fluid includes contacting the additive with water or an aqueous solution, with a method of conforming the formation further including the step of injecting the fluid into the wellbore.

Attorney Docket No. 23267/15

DECLARATION

SOLE/JOINT INVENTOR
ORIGINAL/SUBSTITUTE/CIP

As a below named inventor, I hereby declare that: my residence, post office address, and citizenship are as stated below next to my name. I believe I am the original, first, and sole inventor (if only one name is listed below) or a joint inventor (if plural inventors are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: ***Well Lost Circulation Additive, Lost Circulation Treatment Fluid Made Therefrom, And Method of Minimizing Lost Circulation in a Subterranean Formation*** as described in the specification of **Application Serial No. 08/962,215** filed **October 31, 1997.**

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above; that I do not know and do not believe the same was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to this application; that the invention has not been patented or made the subject of an inventor's certificate issued before the date of this application in any country foreign to the United States of America on an application filed by me or my legal representative or assigns more than twelve months prior to this application; and that I acknowledge the duty to disclose information of which I am aware which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations § 1.56(a). Such information is material when it is not cumulative to information already of record or being made of record in the application, and

(1) it establishes, by itself or in combination with other information, a prima facie case of unpatentability of a claim; or

(2) it refutes, or is inconsistent with, a position the applicant has taken or may take in:

(i) opposing an argument of unpatentability relied on by the Office, or

(ii) asserting an argument of patentability.

I hereby ***do not*** claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificates or provisional priority under Title 35, United States Code § 119(e).

I hereby ***do not*** claim the benefit under Title 35, United States Code § 120.

I HEREBY APPOINT J. M. (MARK) GILBRETH, REG. NO. 33,388, ROBERT W. STROZIER, REG. NO. 34,024 AND LISA KIMES JONES, REG. NO. 41,878 TO PROSECUTE THIS APPLICATION AND TO TRANSACT ALL BUSINESS IN THE PATENT AND TRADEMARK OFFICE IN CONNECTION THEREWITH. PLEASE DIRECT ALL CORRESPONDENCE TO:

GILBRETH & STROZIER, P.C., P.O. Box 61305, Houston, Texas 77208-1305 TEL. 713/ 227-1200.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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